

# Removal of Spray Residue from Apples

C. W. Ellenwood, V. H. Morris, and E. A. Silver



OHIO  
AGRICULTURAL EXPERIMENT STATION  
Wooster, Ohio

## CONTENTS

Acknowledgments .....	2
Introduction .....	3
Plan of the Experimental Work .....	4
Methods of Sampling .....	4
Methods of Analysis .....	5
Accuracy of Analytical Results .....	6
Layout of Spray Plots, 1935 .....	7
Layout of Spray Plots, 1936 .....	7
Varieties Used in Experimental Work .....	8
Amount of Solution Used per Tree .....	9
Dates of Spray Application and Amount of Rainfall .....	9
Relation of Spray Program to Accumulation of Residue at Harvest Time...	10
Residue Removal Results in 1935 .....	13
Variety Factor .....	14
Heating the Wash Solution .....	15
Brushing Compared with Washing .....	17
Effect of Summer Oil in Spray Solutions on Amount of Lead Residue..	17
Washing Twice .....	18
Cost of Washing, 1935 .....	18
Residue Removal Results in 1936 .....	19
Variety Factor .....	22
Types of Washers Compared .....	22
Brushing Compared with Washing .....	25
Value of Wetting Agent in Wash Solution .....	26
Sodium Silicate Combined with Spray Program .....	27
Lead and Arsenic Removal Compared .....	27
Influence of Washing on Storage Qualities .....	29
Lead Found on Unsprayed Apples .....	30
Residue on Fruit at Beginning of Second-brood Spraying, 1936 .....	30
Tandem Washing .....	31
Hydrochloric Acid Used in Washing Apples .....	32
Handling the Acid .....	32
Length of Exposure to Acid Bath .....	33
Method of Testing Wash Solution .....	33
Directions for Making Test of Strength of Acid in Washing Machine	34
Flotation Washers .....	35
Practical Considerations .....	37
Summary .....	38
Literature Cited .....	39

### ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Irwin W. Wander and Manuel Katz who did the major portion of the analytical work reported in this bulletin. Mr. Wander made the analyses in 1935 and Mr. Katz, in 1936.

# REMOVAL OF SPRAY RESIDUES FROM APPLES

C. W. ELLENWOOD, V. H. MORRIS, AND E. A. SILVER

## INTRODUCTION

The removal of spray residue has been a major problem in many apple-growing sections for the past decade. In Ohio the spray programs generally followed by most apple growers include fewer applications of insecticides containing lead and arsenic than do the programs in many other sections. Therefore, there is a much lower residue deposit at harvest time in Ohio than in areas where heavier spraying has been required. There are, however, certain areas in Ohio where the control of insects has become so serious a problem in recent years that it is now necessary to use heavy spray treatments.

In addition to the rather limited area of the State where three broods of codling worms sometimes occur, there are a number of other orchards where it has been necessary to use extreme measures. No insecticide used in the State has been so effective in the control of codling worms as lead arsenate. The substitutes most frequently used in place of lead arsenate contain either arsenic or fluorine, both of which have, as has lead, been subjected to a tolerance by the Federal Food and Drug Administration. The tolerances established by the Federal Food and Drug Administration for 1935 and 1936<sup>1</sup> were 0.018 grain of lead per pound of fruit, 0.01 grain of arsenic trioxide, and 0.01 grain of fluorine.

It is not the purpose of this bulletin to discuss the merit of any particular spray program or the necessity for the establishment of a residue tolerance. The facts are that a tolerance has been established by the Federal Food and Drug Administration and that apples grown in Ohio and shipped out of the State are subject to the regulation.

The Ohio Experiment Station started several years ago to make some preliminary observations on the matter of residue removal and in 1935 initiated a rather extensive study on some phases of the subject. A partial report of the 1935 results was presented in Special Circular 48 (4) of this Station. In 1936 the residue removal work was enlarged to embrace several phases not undertaken in 1935. There are still many other phases of the problem concerning which there is inadequate information and upon which further work is proposed.

It is the purpose of this present discussion to present some of the results of the work undertaken in 1935 and 1936. An effort has been made to determine the probable amounts of residue which result from a number of different spray programs commonly used in Ohio and to determine the effectiveness of methods and equipment which have already become more or less standard in removing the accumulated residue. In presenting the data in this bulletin we have endeavored to keep in mind its possible practical value to the apple growers of Ohio when and if the installation of washing equipment becomes generally necessary.

The results of several hundred analyses made in the Station laboratories and of an even greater number reported in numerous publications have been carefully considered. It is not to be expected that the residues shown in this bulletin for either washed or unwashed samples are an exact measure of the

---

<sup>1</sup>On January 26, 1937, H. A. Wallace, Secretary of Agriculture, set the tolerance for lead, arsenic, and fluorine for 1937 at the 1935 and 1936 figures.

results to be anticipated by individual growers in the State. We believe, however, that the results obtained at Wooster during this 2-year period are representative of what may be expected from similar spray programs and cleaning methods in other parts of the State.

### PLAN OF THE EXPERIMENTAL WORK

There were two main objectives in planning the experiment: (a) to determine the amount of residue which would result from the spray schedules commonly used in Ohio and (b) to determine the effectiveness of removal methods.

Nearly all of the samples analyzed for residue included in the data presented in this bulletin were taken from the Station orchards at Wooster. At the beginning of the seasons of 1935 and 1936 certain portions of the Station orchards were set aside for residue work. Accurate records were kept of the dates the spray material was applied and of the quantity used per tree. Weather conditions were noted each season. All of the trees used were of full bearing age, and moderate to heavy crops of fruit were borne each year. A detailed plan of the arrangement of the plots is presented elsewhere in the bulletin. The spray schedules included in the 2 years' work cover a wide range from those suggested for light infestations of insects to those recommended for areas where codling moth represents a serious problem.

The equipment and solutions used for removing the residue were for the most part already recognized as standard by workers in other states. In a general way, the method of removal in 1935 was considered the most efficient. A 1 to 2 per cent solution of hydrochloric acid heated to 85° to 90° F. in an under brush flood type of washer was the principal method of cleaning used. This system was compared with the conventional type of mechanical brush. In 1936 the same methods of cleaning were again used and a homemade flotation washer was added to the equipment. Vatsol<sup>2</sup>, a wetting agent used to facilitate the action of the acid bath, was used extensively in both the 1935 and 1936 experiments. A more detailed account of the removal methods is presented elsewhere.

### METHODS OF SAMPLING

In order to reduce the errors due to sampling to a minimum, an especial effort was made in 1935 to collect uniform samples of apples. The samples were all collected by one person. A sufficient number of trees in each plot were sampled to give a representative composite sample, and in taking the sample the worker circled the tree. Since size of the fruit and position on the tree affect the quantity of spray residue, apples of medium to under medium size were selected from the lower limbs of the trees. In this way the maximum residue should have been obtained. In a few cases it was necessary to take samples from crates after the apples had been picked, but every effort was made to secure representative samples.

In 1936 the method of taking samples was changed considerably. Duplicate samples were selected directly from the trees as before. The same person selected all of the samples, first picking a set of samples designated as the A samples from the entire series of plots and then picking a second set of samples designated as B samples.

---

<sup>2</sup>Vatsol is a soaplike product made by the American Cyanamid Company. Other similar materials would probably be as effective.

The A and B samples were given residue removal treatments separately and a subsample of each treatment was analyzed.

### METHODS OF ANALYSIS

No detailed description of the analytical methods used in this investigation will be published, as it is felt that few readers will be interested in technique. Outlines are given, but those desiring all the details are referred to the original papers. The procedures are all well known and have been used elsewhere in similar work.

The method for residual lead on sprayed fruit used on the samples taken in 1935 was that developed at the Pennsylvania Experiment Station (5). Residues are dissolved from the fruit by hot dilute hydrochloric acid, and after the removal of organic matter, lead is precipitated as the black sulfide and measured by its reduction of light from a standard source, indicated by readings of a microammeter connected to a photoelectric cell calibrated by known amounts of lead carried through the procedure.

Fourteen hundred grams of apples were weighed out. The stems were cut out and the sepals trimmed off with a sharp scalpel and placed on a perforated filter disk in a funnel. The apples were then washed in a hot (95° C.) solution of 3 per cent (by volume) of concentrated hydrochloric acid and 1 per cent of sodium chloride. This was done by impaling each apple on a sharp-pointed glass stirring rod and immersing it in a beaker containing 500 cc. of the wash solution. After each apple had been immersed about 2 minutes it was held over the funnel containing the stems and sepals and rinsed with an additional quantity of hot wash solution from a wash bottle. The rinse solution was received in a liter volumetric flask. After all the apples in the sample had been washed, the wash and rinse solutions were combined, cooled, made up to a liter, and filtered to remove wax, stems, sepals, and the like.

Aliquot portions of this solution were removed and the organic matter was digested with concentrated sulfuric and nitric acids. After digestion was complete, the solution was diluted, cooled, and neutralized with a solution containing ammonium hydroxide, potassium cyanide, and citric acid. After cooling, the solution was transferred to a Nessler tube placed in the photoelectric colorimeter. After the instrument had been adjusted to take care of any turbidity present, the lead was precipitated by the addition of 6 drops of a 10 per cent solution of sodium sulfide. A reading was obtained on the microammeter and the quantity of lead present determined from the reading by reference to a previously prepared graph of standards.

Although this method was satisfactory in accuracy, convenience, and speed, it seemed desirable, for the 1936 samples, to use the methods preferred by the United States Department of Agriculture Food and Drug Administration (1, 17) which are in general use and which permit the determination of both lead and arsenic in combined alkaline and acid wash liquors used to dissolve the residues from the fruit. After appropriate treatment, the lead was determined colorimetrically as the diphenylthiocarbazone (dithizone) compound in chloroform solution and arsenic, by the Gutzeit method, in which the quantity present is indicated by the depth of brown stain on a mercuric bromide test paper strip exposed to the arsine evolved with hydrogen from pure zinc in the acidulated solution.

Each apple of the 1400-gram sample was immersed in a hot (almost boiling) solution containing 3 per cent sodium hydroxide and 1 per cent sodium oleate until the skin began to check, removed to the funnel, and rinsed with a stream of hot 3 per cent hydrochloric acid. When all the fruit had been thus treated, the alkaline solution was poured through the porcelain filter disk and funnel into the acid rinse solution contained in the flask, and the filter disk, funnel, and beaker were rinsed with more of the acid solution. After cooling, the solution was made to volume.

For the determination of lead in the solution, a 100-cc. aliquot was removed and dewaxed by mixing with 10 cc. of concentrated hydrochloric acid and filtering. Twenty cc. of the filtrate were placed in a 50-cc. Nessler tube to which were added 10 cc. of an ammonia-potassium cyanide-citric acid solution and 20 cc. of a chloroform solution of dithizone. After vigorous shaking, the color of the chloroform layer was compared with that of standards prepared with known amounts of lead.

Arsenic was determined on the same dewaxed solution used for lead. A small aliquot was introduced into the Gutzeit generator. The generator consisted of a 2-oz. widemouthed bottle fitted with a one-hole stopper carrying a 1-cm. inside diameter glass tube 6 to 7 cm. long; into the upper end was inserted a one-hole stopper carrying a glass tube of 2.6 to 2.7 mm. inside diameter and 10 to 12 cm. long. Five cc. of concentrated hydrochloric acid, 5 cc. of a 15 per cent solution of potassium iodide, and 4 drops of a 40 per cent solution of stannous chloride in concentrated hydrochloric acid were added, and the solution was allowed to stand about 10 minutes at 20°-25° C. It was then diluted to 40 cc. with distilled water, and after the addition of 4 grams of granulated zinc, the generator was closed with the remainder of the Gutzeit apparatus which had just previously had a 2-in. piece of Johnson and Johnson dental roll saturated with 20 per cent lead acetate solution inserted into the lower tube; the upper contained a Hanford-Pratt arsenic strip sensitized with mercuric bromide. The assembly was immersed in a water bath at 20° to 25° C. for 1½ hours. The strip was then removed, and the length of the stain was compared with those produced by known amounts of arsenic.

### ACCURACY OF ANALYTICAL RESULTS

The conclusions to be drawn from analytical data obtained in a study of spray residues and residue removal depend to a considerable extent on the accuracy of the determinations. Errors affecting the accuracy are involved in both sampling and the chemical determination. A measure of these combined errors is desirable as an aid in interpreting the results of this study. The duplication of the 1936 samples afforded an opportunity for such a measure. Calculated from the differences between 173 pairs of A and B samples, a standard error of 0.0021 grain of lead per pound of fruit was obtained. The standard error of the difference between the average of the A and B samples representing a spray schedule or residue removal treatment was 0.00308 grain of lead per pound of fruit. For the difference between two treatments to be significant, it should exceed the standard error by two or three times the latter value.

The accuracy of the lead determinations of this study may be compared with that reported by Frear and Hodgkiss (6). In their study of 82 pairs of samples the mean value was 0.02246 grain of lead per pound of fruit, with an average deviation of 0.00152 grain per pound, or 6.8 per cent of the mean. The mean value of the 173 pairs of determinations in this study was 0.0125 grain per pound, with an average deviation of 0.00125 grain of lead per pound, or 10 per cent of the mean.

## LAYOUT OF SPRAY PLOTS, 1935

In 1935 the plots from which samples were to be taken for analyses all received lead arsenate in each of the afterbloom spray applications. There were eight different treatments. All of the plots were sprayed with lead arsenate in the petal-fall spray. Following the petal-fall spray the number of cover sprays ranged from two up to seven. The detailed plan of the plots is presented in Table 1.

TABLE 1.—Layout of Experimental Plots, 1935

Plot	Date of application	Insecticide (L A=lead arsenate)	Plot	Date of application	Insecticide (L A=lead arsenate)
1	June 3.....	L A	6	June 3.....	L A, oil
	June 17.....	L A		June 17.....	L A, oil
	July 29.....	L A		July 1.....	L A
2	June 3.....	L A		July 15.....	L A
	June 17.....	L A		July 29.....	L A
	July 1.....	L A	7	June 3.....	L A, oil
	July 15.....	L A		June 17.....	L A, oil
	July 29.....	L A		July 1.....	L A
	August 12.....	L A		July 15.....	L A
	August 26.....	L A		July 29.....	L A
3	June 3.....	L A, oil		August 12.....	L A
	July 29.....	L A	8	June 3.....	L A, oil
4	June 3.....	L A, oil		June 17.....	L A, oil
	June 17.....	L A		July 1.....	L A
	July 29.....	L A		July 15.....	L A
5	June 3.....	L A, oil		July 29.....	L A
	June 17.....	L A, oil		August 12.....	L A
	July 1.....	L A		August 26.....	L A
	July 29.....	L A			

In all of the plots except 1 and 2, summer oil (at the rate of  $\frac{1}{2}$  per cent) was added as a supplement to the lead arsenate. Plots 3 and 4 received oil in the 10-day spray. Plots 5, 6, 7, and 8 received oil in two applications made 10 and 24 days after petal fall. It will be seen then that the spray treatments of the several plots in 1935 ranged from what would be considered average control measures to those used under heavy codling moth infestations. Lead arsenate was used throughout the season at the rate of  $2\frac{1}{2}$  pounds to 100 gallons of solution. Hydrated lime with a relatively high magnesium content was used in connection with the lead arsenate in each of the applications at the rate of 5 pounds per 100 gallons of solution.

## LAYOUT OF SPRAY PLOTS, 1936

In 1936 the spray treatment on the 19 plots used in the residue work (Table 2) differed considerably from the plan followed in 1935, although some of the treatments used in 1935 were duplicated. The spray treatments in 1936 embraced several plots which contained insecticides sometimes used as substitutes for or supplements to the conventional lead arsenate schedules. In general, these 19 plots ranged from a minimum of two cover sprays, one 3 weeks after petal fall and another in late July, up to as many as seven cover sprays. The substitutes used for lead arsenate were calcium arsenate and zinc arsenate. Summer oil was used as a supplement to the lead arsenate in the application



made 3 weeks after petal fall in five plots. In Plot 9 summer oil was used supplementary to the regular lead arsenate schedule in the applications made 3 and 5 weeks after petal fall. Lead arsenate, calcium arsenate, and zinc arsenate were used at the rate of 2½ pounds to 100 gallons of solution except in Plot 17, where the strength of lead arsenate was reduced to 2 pounds to 100 gallons in the last cover spray. Plots 7 and 8 were sprayed with calcium arsenate in the petal-fall spray. All the other plots were sprayed with lead arsenate at that time.

TABLE 2.—Layout of Experimental Plots, 1936

Plot	Date of application	Insecticide*	Plot	Date of application	Insecticide*
1	June 3..... July 29.....	L A C A		July 15..... July 29..... August 12..... August 26.....	L A C A C A C A
2	June 3..... July 29.....	L A, oil C A			
3	June 3..... July 29.....	L A L A	11	June 3..... June 17..... July 1..... July 29.....	L A L A L A C A
4	June 3..... June 17..... July 29.....	L A L A C A	12	June 3..... June 17..... July 29.....	L A L A Z A
5	June 3..... June 17..... July 29.....	L A, oil L A C A	13	June 3..... June 17..... July 29.....	L A L A L A
6	June 3..... June 17..... July 29.....	L A, oil L A L A		(Sprayed with sodium silicate 1 week before picking)	
7	June 3..... June 17..... July 29.....	C A C A C A	14	June 3..... June 17..... July 29.....	L A L A L A, sodium silicate
8	June 3..... June 17..... July 1..... July 29.....	C A C A C A C A	15	June 3..... July 29.....	L A Z A
9	June 3..... June 17..... July 1..... July 15..... July 29..... August 12..... August 26.....	L A, oil L A, oil L A L A L A L A L A	16	June 3..... July 29.....	L A nicotine, oil
			17	June 3..... July 29.....	L A L A (2 lb. to 100 gal.)
10	June 3..... June 17..... July 1.....	L A, oil L A L A	18	Same as 17, except high-calcium lime was used	
			19	June 3..... July 29.....	L A L A (fish oil sticker)

\*L A=lead arsenate; C A=calcium arsenate; Z A=zinc arsenate.

Hydrated lime at the rate of 5 pounds per 100 gallons of solution was used in connection with the insecticide throughout the season. The lime used on all plots except 18 was manufactured in Ohio and contained relatively high proportions of magnesium. The lime used on Plot 18 was manufactured in Pennsylvania and was higher in calcium and lower in magnesium than the Ohio lime.

#### VARIETIES USED IN EXPERIMENTAL WORK

The varieties included in the experimental work at Wooster in 1935 were McIntosh, Grimes, Jonathan, and Stayman Winesap<sup>3</sup> in Orchard K; these trees had been planted in 1922. Baldwin trees planted in 1916 were located in Orchard D.

<sup>3</sup>For convenience Stayman Winesap will hereafter be termed Stayman in this bulletin.

In 1936 all the trees in Orchard K and the Baldwin and Stayman trees in Orchard D were again used in the spray plots set aside for residue work. In addition, the Delicious and Stayman trees in Orchard C planted in 1915, 35-year-old Delicious and Stayman trees in Orchard B, and Stayman trees 15 years old in Orchard J were used in the layout of the 1936 residue work. In 1935 264 trees were sprayed with the several solutions used in the residue work and in 1936, 430 trees were included. In 1935 there were eight different spray treatments ranging from one to seven cover sprays. In 1936 there were 19 separate plots.

The varieties used for analysis cover a range of season from McIntosh (late autumn) to Stayman, which is usually picked about the middle of October. Grimes and Jonathan are two of the smaller-sized varieties; the other varieties average medium in size.

#### AMOUNT OF SOLUTION USED PER TREE

The average amount of spray material used an application for the cover sprays of these trees is shown in Table 3.

TABLE 3.—Gallons of Spray Solutions Applied a Tree per Application for Cover Sprays

Year	Age of trees		
	14-15 years	20-22 years	35 years
1935.....	<i>Gal.</i> 9 to 11	<i>Gal.</i> 19 to 20	<i>Gal.</i> .....
1936.....	10 to 15	18 to 25	21 to 28

The amount of solution used per tree was enough to insure good coverage, but no attempt was made to drench the trees. To secure as much uniformity as possible, the same crew of two men applied the solution throughout the plots each year. The spraying was done in the forenoon to take advantage of the calmest part of the day.

#### DATES OF SPRAY APPLICATION AND AMOUNT OF RAINFALL

The dates the several applications of spray solution were applied and the rainfall for the period between the first application and the date the apples were picked are presented in Tables 4 and 5. The dates of applying the solu-

TABLE 4.—Dates of Spray Application and Rainfall During Growing Season, 1935

Interval between sprays	Amount of rainfall	Interval between sprays	Amount of rainfall
	<i>In.</i>		<i>In.</i>
June 3 (1st cover) to June 17 (2nd cover) .....	0.55	Sept. 14 to Sept. 25 (Grimes picking date) .....	0.00
June 17 to July 1 (3rd cover) .....	3.87	Sept. 25 to Sept. 30 (Jonathan picking date) .....	0.88
July 1 to July 15 (4th cover) .....	3.38	Sept. 30 to Oct. 11 (Baldwin picking date) .....	0.62
July 15 to July 29 (5th cover) .....	5.28	Oct. 11 to Oct. 15 (Stayman picking date) .....	0.46
July 29 to Aug. 12 (6th cover) .....	7.92		
Aug. 12 to Aug. 26 (7th cover) .....	0.54	Total (135 days) .....	25.03
Aug. 26 to Sept. 14 (McIntosh picking date) .....	1.53		

TABLE 5.—Dates of Spray Application and Rainfall During Growing Season, 1936

Interval between sprays	Amount of rainfall	Interval between sprays	Amount of rainfall
	<i>In.</i>		<i>In.</i>
June 3 (1st cover) to June 17 (2nd cover) .....	0.87	Sept. 17 to Sept. 22 (Jonathan picking date) .....	0.00
June 17 to July 1 (3rd cover) .....	1.49	Sept. 22 to Sept. 28 (Delicious picking date) .....	1.22
July 1 to July 15 (4th cover) .....	2.62	Sept. 28 to Oct. 4 (Baldwin picking date) .....	1.27
July 15 to July 29 (5th cover) .....	2.25	Oct. 4 to Oct. 9 (Stayman picking date) .....	0.54
July 29 to Aug. 12 (6th cover) .....	1.24		
Aug. 12 to Aug. 26 (7th cover) .....	1.77		
Aug. 26 to Sept. 8 (McIntosh picking date) .....	1.93		
Sept. 8 to Sept. 17 (Grimes picking date) .....	0.14	Total (129 days) .....	15.34

tion were exactly the same both years. The petal-fall spray, which is not taken into consideration in Tables 4 and 5, was applied slightly earlier in 1936 than in 1935. Picking started and finished earlier in 1936 than in 1935. It will be noted that there was a period of very heavy precipitation in the early mid-summer of 1935 but that the latter part of the summer was very dry. During the season of 1936 the total precipitation was considerably less than in 1935 but was more evenly distributed.

#### RELATION OF SPRAY PROGRAM TO ACCUMULATION OF RESIDUE AT HARVEST TIME

There are so many variable factors involved that it is not possible to anticipate definitely the amount of residue which will result from following any particular spray program. Besides the kind and strength of spray materials used, probably the most variable factor in determining the amount of residue is the dosage of spray solution per tree. Rainfall and other weather factors also have an influence on the residue remaining at harvest time. During the seasons of 1935 and 1936, 21 different spray programs were used. Nineteen of these are summarized in Tables 6 and 7. By reference to Tables 3, 4, and 5 some idea of the dosage and weather conditions for the two seasons can be gained. It is not suggested here that the residues shown by the analyses made in these 2 years from the apples harvested at Wooster can be used as an inflexible guide to the probable amount of residue which will result elsewhere in the State from any or all of the several programs. It will be noted that the same spray programs resulted in somewhat varying quantities of residue in 1935 and 1936. However, after examining in detail the results of a large number of analyses made at the Station we are inclined to believe that where thorough spraying is done the residue will generally not vary significantly from the figures shown in these tables. The results of analyses in southern Ohio reported by Porter (14) were very similar to those shown in the foregoing tables. From the data included in Tables 6 and 7 and those of Porter, as well as from analyses made at the Station of numerous samples collected at random from other sources, it seems possible to draw some practical conclusions:

TABLE 6.—Relation of Spray Program to Residue Occurring at Harvest Time at Wooster

(Lead arsenate used as only insecticide; unwashed samples)

Spray program	No. of cover sprays		Grain of lead per pound of fruit at harvest time					
	Before July 2	After July 2	McIntosh	Grimes	Jona- than	Stay- man	Delic- ious	Bald- win
Lead arsenate 2½-100 in first cover; lead arsenate 2-100 in second cover, 1936.....	1	1	.....	.....	.....	0.020	.....	.....
Lead arsenate 2½-100, 1936....	1	1	0.022	0.029	0.028	0.024	.....	.....
Lead arsenate 2½-100 plus oil in first cover, 1935 .....	1	1	0.039	0.037	0.047	0.021	.....	0.026
Lead arsenate 2½-100, 1935....	2	1	0.035	.....	0.035	0.039	.....	.....
1936.....	2	1	.....	.....	.....	0.038	.....	0.034
Lead arsenate 2½-100, 1935....	2	1	0.034	0.044	0.046	0.036	.....	.....
oil in second cover 1936....	2	1	0.028	0.040	0.032	0.029	.....	.....
Lead arsenate 2½-100, oil in second and third covers, 1935	3	1	0.054	0.050	0.056	0.056	.....	.....
Lead arsenate 2½-100, oil in second and third covers, 1935	3	2	0.060	0.068	0.062	0.076	.....	0.093
Lead arsenate 2½, oil in second and third covers, 1935	3	3	0.119	0.074	0.100	0.110	.....	0.128
Lead arsenate 2½-100, 1935....	3	4	0.132	0.135	0.130	0.139	.....	.....
Lead arsenate 2½-100, oil in second and third covers, 1935	3	4	0.116	0.175	0.150	0.155	.....	0.106
1936	3	4	.....	.....	0.110	0.075	0.115	.....

1. Any spray program which includes lead arsenate used at the rate of 2 pounds or more per 100 gallons of solution much later than July 1 may be expected to exceed the 1936 Federal lead tolerance (0.018).

2. Where calcium arsenate or zinc arsenate is substituted for lead arsenate in the sprays applied after July 1, provided lead arsenate is not applied much later than June 15, the lead residue at harvest time will be slightly under the 1936 lead tolerance (0.018). However, it must be stated that if more than two lead arsenate sprays are applied between the petal-fall spray and July 1, the lead residue is very likely to exceed the 1936 tolerance.

3. If the use of lead arsenate is continued into the early part of July with a total of as many as four cover sprays of this material, as is sometimes necessary in badly worm-infested orchards, the lead residue may considerably exceed the lead tolerance even though some substitute for lead arsenate is used in the remaining sprays.

4. The total amount of residue increases in proportion to the number of sprays applied, particularly late in the year.

5. When oil was added to first, second, or third cover sprays there was no significant increase in the amount of lead remaining at harvest time.

6. Heavy rainfall, no doubt, tends to reduce the residue at harvest time but even abnormally heavy precipitation is not sufficient insurance against residues in excess of the present tolerance. It will be noted that in spite of a much heavier precipitation in 1935 than in 1936 the lead residue in 1935 was greater than in 1936. It is suggested that the spray solution may adhere to

TABLE 7.—Relation of Spray Program to Residue Occurring at Harvest Time at Wooster, 1936

(Lead arsenate and substitute materials used as insecticides at the rate of 2% lb. to 100 gal.; unwashed samples)

Spray program	Total number of cover sprays	Grain of lead per lb. of fruit at harvest time					
		McIntosh	Grimes	Jona- than	Stay- man	Delic- ious	Bald- win
Petal-fall and 1st cover lead arsenate; last cover calcium arsenate ....	2	0.008	0.010	0.010	0.010	.....	.....
Petal-fall lead arsenate; 1st cover lead arsenate plus oil; last cover calcium arsenate.....	2	0.009	0.009	0.011	0.010	.. ...	.....
Petal-fall and 2nd cover lead arsenate; last cover calcium arsenate ....	2	0.012	0.013	0.007	0.011	.....	.....
Petal-fall lead arsenate; 1st cover lead arsenate plus oil; 2nd cover lead arsenate; last cover calcium arsenate .....	3	0.012	0.018	0.016	0.017	.....	.....
Petal-fall lead arsenate; 1st cover lead arsenate plus oil; 2nd, 3rd, and 4th covers lead arsenate; 5th, 6th, and 7th covers calcium arsenate ....	7	.....	.....	0.024	0.030	0.020	.....
Petal-fall and 3rd cover sprays lead arsenate; 4th cover calcium arsenate	4	.....	.....	.....	0.020	0.020	.....
Petal-fall and 2nd cover sprays lead arsenate; 3rd cover zinc arsenate....	3	.....	.....	.....	0.012	0.012	.....
Petal-fall and 1st cover lead arsenate; last cover zinc arsenate .....	2	.....	.....	.....	0.020	.....	.....
Petal-fall, 1st cover, and last cover, lead arsenate.....	2	.....	.....	.....	0.007	.....	.....

the fruit more in years when there are periods of excessive moisture which may serve to prolong the colloidal condition of the spray solution. Such weather conditions do check the mechanical formation of flakes and slow up the process of flaking, which is supposedly promoted by the inclusion of large proportions of lime in the average summer spray program in Ohio. From the results of these 2 years it may be concluded that it is not wise for Ohio growers to put too much dependence on heavy rainfall as a means of eliminating spray residue. This conclusion is supported by the work of Frear and Worthley (7) in Pennsylvania. These workers questioned whether heavy, concentrated downpours of rain were as effective in removing spray residues as more gentle rains scattered throughout the growth period of the fruit. They found that samples analyzed after heavy September rains showed surprisingly little reduction in spray residues.

7. Arsenic residue on the apples at harvest time in 1936 (Table 8) exceeded the tolerance in seven of the 10 plots from which samples were analyzed. The arsenic residues on the samples from Plots 3, 4, and 13 were, respectively, 0.010, 0.009, 0, and 0.008. The results from these three plots are all so close to the tolerance, 0.01, as to indicate that the spray treatments followed on them in 1936 could not safely be suggested as a means of avoiding excessive arsenic residues.

TABLE 8.—Relation of Spray Program to Residue Occurring at Harvest Time  
Variety Stayman; samples from Station Orchard, 1936; unwashed samples

Spray program	No. of cover sprays		Grain of arsenic (As <sub>2</sub> O <sub>3</sub> ) per lb. of fruit at harvest time	Grain of lead per lb. of fruit
	Before July 2	After July 2		
Lead arsenate plus oil, 1st cover; calcium arsenate, last cover.....	1	1	0.011	0.010
Lead arsenate, 1st cover; lead arsenate, last cover ...	1	1	0.010	0.024
Lead arsenate, 1st cover; lead arsenate, 2nd cover; calcium arsenate, last cover.....	2	1	0.009	0.011
Lead arsenate plus oil, 1st cover; lead arsenate, 2nd cover; lead arsenate, last cover .....	2	1	0.012	0.020
Calcium arsenate, 1st cover; calcium arsenate, 2nd cover; calcium arsenate, 3rd cover; calcium arsenate, last cover .....	3	1	0.019	.....
Lead arsenate plus oil, 1st cover; lead arsenate plus oil, 2nd cover; lead arsenate, 3rd cover; lead arsenate, 4th cover; lead arsenate, 5th cover; lead arsenate, 6th cover; lead arsenate, 7th cover .....	3	4	0.031	0.075
Lead arsenate plus oil, 1st cover; lead arsenate, 2nd cover; lead arsenate, 3rd cover; lead arsenate, 4th cover; calcium arsenate, 5th cover; calcium arsenate, 6th cover; calcium arsenate, 7th cover.....	3	4	0.033	0.030
Lead arsenate, 1st cover; lead arsenate, 2nd cover; lead arsenate, 3rd cover; calcium arsenate, last cover .....	3	1	0.031	0.020
Lead arsenate, 1st cover; lead arsenate, 2nd cover; zinc arsenate, last cover .....	2	1	0.026	0.012
Lead arsenate, 1st cover; lead arsenate, 2nd cover; lead arsenate, last cover. Sprayed with sodium silicate 1 week before picking.....	2	1	0.008	0.028

8. The arsenic residue on the fruit receiving seven cover sprays in the last three of which calcium arsenate was substituted for lead arsenate did not materially differ from that on the plots where seven cover sprays of lead arsenate were applied.

#### RESIDUE REMOVAL RESULTS IN 1935

The results secured from removing residue by washing and wiping in 1935 are presented in Tables 9 and 10. Only analyses for lead were made. All the washing was done with a Bean under brush flood type washer<sup>4</sup>. Most of the apples were washed in a hydrochloric acid solution ranging from 1½ to 2 per cent heated to 85° or 90° F. To this solution 5 pounds of vatsol and 6 to 8 pints of anti-foam per 100 gallons were added.

The unwashed samples of each variety from all of the plots (Table 9) were well above the 1935 lead tolerance, 0.018. The amount of lead on the unwashed samples increased progressively according to the number of cover sprays. The lightest load of lead, 0.021, occurred on Stayman which had received two cover sprays and the heaviest, 0.175, on Grimes which had been given seven cover sprays with lead arsenate plus oil. All of the washed apples except one sample of Jonathan from a plot which had received three cover sprays were

<sup>4</sup>The washer used was Model E made by the John Bean Mfg. Co., Lansing, Mich.

well under the tolerance. In the case of this particular Jonathan sample there was reason to think that a mistake had been made in sampling. The sampling procedure in 1936, discussed elsewhere, differed considerably from that of 1935 and was no doubt much more exact.

TABLE 9.—Residue Removal, 1935

Lead arsenate used as insecticide; supplemented with oil in six plots; under brush flood type washer used

Spray treatment		Washing treatment*	Lead residue, grain of lead per lb. of fruit				
No. of cover sprays	No. of oil applications		McIntosh	Grimes	Jonathan	Stayman	Baldwin
2	1	Not washed	0.039	0.037	0.047	0.042	0.026
2	1	Washed once	.006	.005	.015	.006	.005
3	0	Not washed	.035	.075	.035	.039	.....
3	0	Washed once	.006	.006	.012	.006	.....
3	1	Not washed	.034	.044	.046	.036	.....
3	1	Washed once	.007	.007	.026	.006	.....
4	2	Not washed	.054	.050	.056	.056	.....
4	2	Washed once	.008	.009	.014	.007	.....
5	2	Not washed	.060	.068	.062	.076	.093
5	2	Washed once	.008	.008	.010	.009	.013
6	2	Not washed	.119	.074	.100	.110	.128
6	2	Washed once	.009	.009	.016	.012	.008
7	2	Not washed	.116	.175	.150	.110	.106
7	2	Washed once	.008	.011	.011	.012	.008
7	2	Washed twice	.007	.008	.010	.....	.007
7	2	Wiped once	.....	.....	.084	.091	.066
7	2	Wiped once and washed once	.....	.....	.015	.....	.016
7	2	Wiped once and washed twice	.....	.....	.012	.....	.....
7	0	Not washed	.132	.135	.130	.139	.....
7	0	Washed once	.009	.007	.012	.009	.....
7	0	Washed twice	.006	.009	.014	.....	.....

\*Washing solution consisted of 1½ to 2 per cent hydrochloric acid solution plus vatso and anti-foam heated to 85° to 90° F.; apples washed within 4 days after picking.

TABLE 10.—Range of Lead Residue from Two to Seven Cover Sprays

Grain of lead per pound

Variety	Before washing		After washing	
	Highest residue	Lowest residue	Highest residue	Lowest residue
McIntosh.....	0.132	0.035	0.009	0.006
Grimes.....	0.175	0.037	0.011	0.005
Jonathan.....	0.150	0.035	0.016	0.010
Stayman.....	0.110	0.021	0.013	0.005

#### VARIETY FACTOR

There was considerable difference in the amount of residue on the several varieties used in the 1935 work. These differences are due to several factors. Difference in size is, no doubt, the main reason for variation in quantity of residue on the different varieties but the amount of russet on the skin, whether natural or mechanical, and the degree of waxiness are other contributing

factors. Date of picking probably has a bearing on the lead load but there was generally lighter residue on McIntosh picked September 14 than on Jonathan picked September 30. Of the four varieties which were included in all of the plots in 1935 (McIntosh, Grimes, Jonathan, and Stayman), the lead residue was lightest on the unwashed McIntosh (Fig. 1). Then, in increasing amounts, unwashed samples of the other varieties ranked in this order—Stayman, Jonathan, and Grimes. The amount of lead on the washed apples was practically the same on McIntosh, Grimes, and Stayman and all of these varieties had considerably less lead residue than Jonathan, even though the sample of washed Jonathan which showed a residue of 0.026 is eliminated from consideration. It was obvious that residue was considerably more difficult to remove from Jonathan than from the other varieties. This was probably due, in part at least, to considerable russetting on the Jonathan in 1935.

**Lead Residue Resulting from a  
Different Number of Cover Sprays.  
Lead Arsenate Used in Each Spray.  
Variety, McIntosh — 1935.**

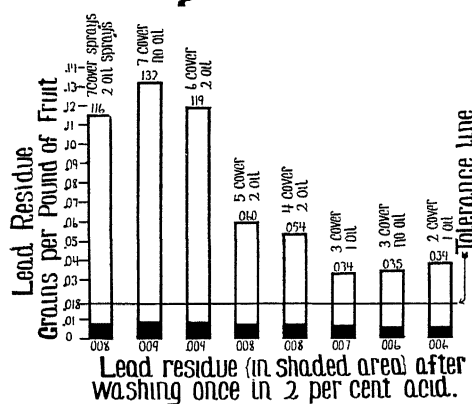


Fig. 1.—Lead residue on McIntosh and results of washing

Baldwin (Fig. 3) was not represented in all of the plots. There were practically the same amounts of residue on the unwashed and washed samples of Baldwin as were found on comparable plots of washed and unwashed Stayman.

In Table 10 is presented a condensed summary of the range of lead found on the several varieties in the 1935 plots.

#### HEATING THE WASH SOLUTION

Heating the acid solution to 85° to 90° F. improved its efficiency appreciably. A temperature of 100° to 110° F. has been suggested as giving best results, but the heating device available for use at the Station would not raise

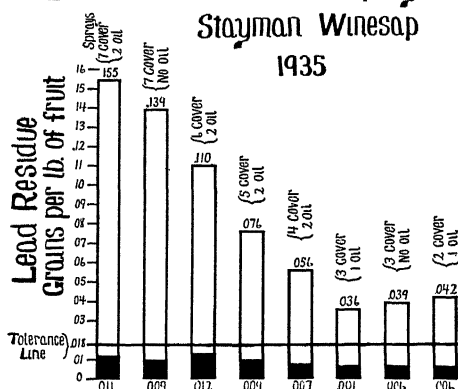


### Lead Residue Resulting from a Different Number of Cover Sprays.

Lead Arsenate in each Spray.

Stayman Winesap

1935



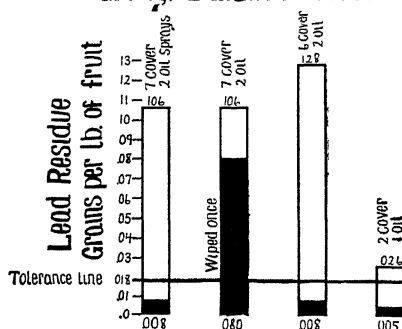
Lead residue (in shaded area) after  
washing once with 2 per cent acid.

Fig. 2.—Lead residue on Stayman and  
results of washing

### Lead Residue Resulting from a Different Number of Cover Sprays

Lead Arsenate in each Spray.

Variety, Baldwin—1935.



Lead residue (in shaded area) after  
washing once with 2 per cent acid

Fig. 3.—Lead residue on Baldwin and  
results of washing

the temperature of the solution above 90° F. The results of washing in heated and normal hydrant-temperature (55° to 60° F.) acid solutions are shown in Table 11.

**TABLE 11.—Influence of Temperature of Washing Solution on Lead Removed**  
Grain of lead per pound

Variety	Amount of lead before washing	Amount of lead after washing once, 2% HCl, Temp., 55°-60° F.	Amount of lead after washing once, 2% HCl, Temp., 85°-90° F.
Baldwin.....	0.026	0.007	0.005
Baldwin.....	0.093	0.012	0.008
Baldwin.....	0.128	0.012	0.008

The heating device used in connection with the under brush flood type washer at Wooster consisted of a coil of 3/8-inch copper pipe 50 feet long placed in the acid compartment through which live steam passed. The steam was generated in a boiler with a capacity of about 10 gallons of water placed in a horizontal position alongside the washer. The boiler was heated by natural gas. This homemade heating device was built at a cost of \$12. The boiler and gas burner were secondhand. The copper pipe, fire brick, and the asbestos covering for the boiler were new.

#### BRUSHING COMPARED WITH WASHING

Results of brushing<sup>5</sup> as compared with washing apples given the same spray treatment are presented in Table 12. Brushing removed 17 to 44 per cent of the total lead deposit and washing, more than 90 per cent. Only in relatively low-residue samples was the mechanical brush effective in cleaning apples.

**TABLE 12.—Brushing Compared with Washing, 1935**  
Grain of lead per pound

Variety	Amount of lead before treatment	Amount of lead after brushing	Per cent of lead removed by brushing	Amount of lead after washing once	Per cent of lead removed by washing
Jonathan.....	0.150	0.084	44.0	0.011	92.6
Baldwin.....	0.106	0.080	24.5	0.008	92.4
Stayman.....	0.110	0.091	17.3	0.009	91.8

#### EFFECT OF SUMMER OIL IN SPRAY SOLUTIONS ON AMOUNT OF LEAD RESIDUE

The addition of summer oil to the first and second cover sprays seemed to increase the lead load only slightly. Cleaning the fruit was not made appreciably more difficult by the addition of oil in these early summer sprays. Doubtless, had the oil been applied in the late summer sprays, larger deposits of lead would have been present on the unwashed samples and the removal would have been more difficult.

<sup>5</sup>The mechanical brush used was the Bean two-way cleaner made by the John Bean Mfg. Co.

## WASHING TWICE

In connection with the washing operations in 1935 a number of samples were run through the washer a second time and an analysis was made of the lead residue. The comparison between these samples and other samples given the same spray treatment but washed only once is presented in Table 13. Generally, the lead load was slightly reduced by the second washing but it will be noted that in every case one washing had reduced the lead load well below the tolerance. The extra expense of the second washing was not justified by the results in 1935. Most of the samples shown in Table 13 carried very high loads of lead before washing but washing once brought the residue well under the tolerance permitted. It may be noted from this table that the efficiency of a single washing ranged from 73 to 95 per cent removal.

TABLE 13.—Washing Once and Twice, 1935

Variety	Amount of lead residue (Gr. per lb. of fruit)			Per cent of lead removed by washing	
	Before washing	After washing once	After washing twice	Once	Twice
McIntosh.....	0.132	0.009	0.006	94	96
McIntosh.....	0.116	0.008	0.007	93	94
Grimes.....	0.135	0.007	0.009	95	93
Grimes.....	0.175	0.011	0.008	94	95
Jonathan.....	0.150	0.011	0.010	93	94
Jonathan.....	0.130	0.012	0.014	91	90
Baldwin.....	0.026	0.007	0.006	73	77
Baldwin.....	0.128	0.014	0.010	89	92
Baldwin.....	0.106	0.012	0.007	89	93

## COST OF WASHING, 1935

The cost of washing in 1935, not including labor for operation of the washer, was 2½ cents per bushel. This cost included the price of the acid, which was \$2.45 per cwt. for relatively small quantities of 18° hydrochloric acid. Vatsol cost 45 cents per pound and anti-foam, \$1.00 per gallon. Other items of cost included were depreciation on washer and motor, electric current, and gas used for heating the solution.

The washing machine was hooked up in connection with the sizing equipment and very little additional labor was required. The capacity of the washing machine did not exceed 40 bushels per hour. Operating costs per bushel would, no doubt, be less on a machine with greater capacity. The cost of the washing operation will naturally vary with the amount and nature of the residue deposit, the volume of fruit to be washed, and many other local factors. Where the deposit is exceptionally heavy and especially where the residue is accompanied by an adhesive sticker or oil, it may be necessary to use tandem washers or to run the apples through a washer twice. Under such conditions the cost of washing is naturally somewhat greater. Haller, Smith, and Ryall (10) have estimated the cost of washing to range from 1 to 5 cents per bushel; Hough, et al (11) in Virginia have placed the operating cost for washing between 2½ and 6 cents per barrel and the cost of washing apples taken from storage at from 12 to 15 cents per barrel.

## RESIDUE REMOVAL RESULTS IN 1936

The results of the 1936 residue removal experimental work are shown in Tables 14 to 19. Generally, the lead residue was not quite as heavy at picking time in 1936 as it was in 1935 on comparable plots. The layout of the plots in 1936, as has been pointed out elsewhere, differed considerably from the 1935 plan. Approximately 500 individual samples were analyzed in 1936 as compared with 150 in 1935. The amount of residue remaining after washing in 1936 did not differ materially from that of 1935. A higher percentage of the 1936 than of the 1935 washed samples had a residue of 0.005 grain or less of lead per pound of fruit, but it should be stated that there were a good many of the 1936 plots on which substitutes for lead arsenate were used in part or all of the applications.

TABLE 14.—Residue Removal, 1936. Plots 1 to 6  
Varieties: McIntosh, Grimes, Jonathan, and Stayman. All plots  
sprayed with lead arsenate at petal fall

Plot	Spray treatment Cover sprays	Washing treatment			Lead residue (Gr. per lb. of fruit)			
		Strength of acid	Tempera- ture of solution	Type of washer	McIn- tosh	Grimes	Jona- than	Stay- man
1	Lead arsenate, June 3.....	<i>Pct.</i>		Not washed	0.008	0.010	0.010	0.010
	Calcium arsenate, July 29.....	1	Hydrant	Under brush flood	.004	.005	.005	.006
2	Lead arsenate plus oil, June 3.....			Not washed	.009	.009	.011	.010
	Calcium arsenate, July 29.....	1	Hydrant	Under brush flood	.005	.003	.006	.005
3	Lead arsenate, June 3.....	1	Hydrant	Not washed	.022	.029	.028	.024
				Under brush flood	.005	.006	.006	.....
	Lead arsenate, July 29.....	1 plus vatsol	Hydrant	Under brush flood	.006	.005	.005	.008
4				Wiped	.017	.020	.020	.027
	Lead arsenate, June 3.....			Not washed	.012	.013	.007	.015
5	Lead arsenate, June 17.....							
	Calcium arsenate, July 29.....	1	Hydrant	Under brush flood	.005	.005	.005	.004
6	Lead arsenate, oil, June 3.....			Not washed	.012	.018	.016	.017
	Lead arsenate, June 17.....							
6	Calcium arsenate, July 29.....	1	Hydrant	Under brush flood	.005	.005	.006	.004
	Lead arsenate, oil, June 3.....			Not washed	.028	.040	.032	.029
6	Lead arsenate, June 17.....	1	Hydrant	Under brush flood	.006	.004	.006	.....
	Lead arsenate, July 29.....	1 plus vatsol	Hydrant	Under brush flood	.007	.007	.007	.006
6				Wiped	.020	.024	.027	.029

TABLE 15.—Residue Removal, 1936. Plot 8, Variety Stayman

Trees sprayed with calcium arsenate throughout season  
beginning with petal fall

Plot	No. of cover sprays calcium arsenate	Washing treatment			Arsenical residue, grain of As <sub>2</sub> O <sub>3</sub> per lb. of fruit	Per cent of residue removed
		Strength of acid solution	Tempera- ture	Type of washer		
8	C A, June 3	<i>Pct.</i> *	.....	.....	0.019	.....
	C A, June 17					
	C A, July 1 C A, July 29	1	Hydrant	Under brush flood	0.005	68.4

\*Not washed.

TABLE 16.—Residue Removal, 1936. Plots 9 and 10—Heavy Spray Schedule

Varieties: Jonathan, Delicious, and Stayman. Plots sprayed  
with lead arsenate in petal fall

Plot	No. of cover sprays	Washing treatment			Lead residue, grain per lb. of fruit		
		Solution	Tempera- ture	Type of washer	Jona- than	Delic- ious	Stay- man
9	L A, oil, June 3	<i>Pct.</i> Not washed	° F. .....	.....	0.071	0.093	0.075
	L A, oil, June 17						
	L A, July 1	1	Hydrant	Under brush flood	.008	.006	.009
	L A, July 15	1	85-90	Under brush flood	.012	.005	.008
	L A, July 29	1	Hydrant	Flotation	.026	.018	.009
	L A, August 12	1½	Hydrant	Under brush flood	.009	.012	.012
10	L A, oil, June 3	Not washed	.....	.....	.024	.020	.030
	L A, June 17						
	L A, July 1	1	Hydrant	Under brush flood	.007	.005	.009
	L A, July 15	1	85-90	Under brush flood	.008	.004	.007
	C A, July 29	1	Hydrant	Flotation	.009	.009	.015
	C A, August 12	1½	Hydrant	Under brush flood	.005	.005	.006

TABLE 17.—Residue Removal, 1936. Plots 11 and 12

Varieties: Delicious and Stayman. Trees sprayed with  
lead arsenate in petal fall

Plot	Cover sprays	Washing treatment			Lead residue, grain per lb. of fruit	
		Solution	Tempera- ture	Type of washer	Delicious	Stayman
11	L A, June 3	<i>Pct.</i> Not washed	.....	.....	0.020	0.020
	L A, June 17	1	Hydrant	Under brush flood	0.006	0.015
	L A, July 1					
	C A, July 29	1	Hydrant	Flotation	0.008	0.009
12	L A, June 3	Not washed	.....	.....	0.012	0.012
	L A, June 17	1	Hydrant	Under brush flood	0.005	0.007
	Z A,* July 29	1	Hydrant	Flotation	0.005	0.007

\*Z A=zinc arsenate.

TABLE 18.—Residue Removal, 1936. Plot 13  
 Varieties: Baldwin and Stayman. Trees sprayed with lead  
 arsenate in petal fall

Plot	Cover sprays	Washing treatment			Lead residue, grain per lb. of fruit	
		Solution	Temperature	Type of washer	Baldwin	Stayman
13	L A, June 3 L A, June 17 L A, July 29  Sprayed with sodium silicate 1 week before picking	<i>Pct.</i> Not washed before spraying with sodium silicate	.....	.....	0.034	0.038
		Not washed but sprayed with sodium silicate	.....	.....	0.022	0.028
		1	Hydrant	Under brush flood	0.003	0.006
		1	Hydrant	Flotation	0.009	0.010

TABLE 19.—Residue Removal, 1936. Plots 15 to 19  
 Variety Stayman. Sprayed with lead arsenate in petal fall

Plot	Cover sprays	Washing treatment			Lead residue, grain per lb. of fruit
		Solution	Temperature	Type of washer	
15	L A, June 3 Z A, July 29	<i>Pct.</i> Not washed	.....	.....	0.020
		1	Hydrant	Under brush flood	.005
16	L A, June 3 Nicotine oil, July 29	1	Hydrant	Under brush flood	.007
		1	Hydrant	Flotation	.004
17	L A, 2½ lb. to 100, June 3 L A, 2 lb. to 100, July 29	Not washed	.....	.....	.020
		1	Hydrant	Under brush flood	.005
18	L A, 2½ lb. to 100, June 3 L A, 2 lb. to 100, July 29 high-calcium lime	1	Hydrant	Under brush flood	.006
		1	Hydrant	Flotation	.006
19	L A, June 3 L A, fish oil, July 29	Not washed	.....	.....	.030
		1	Hydrant	Under brush flood	.007
		1	Hydrant	Flotation	.010

In 1936 removal by a flotation washer was compared with the under brush flood washer, as well as the mechanical brush used in 1935. Influences of a number of factors on the efficiency of washing operations are discussed in some detail in the following pages.

The data shown in Tables 14 to 19 are from samples of apples taken from the Station orchard spray plots outlined previously in this bulletin. Enough samples from commercial orchards were analyzed to indicate that the results shown in these tables were representative of conditions in Ohio in 1936 under comparable spray programs.

## VARIETY FACTOR

There was much less variation in the residue deposits on different varieties in 1936 than in 1935. In Table 20 is presented a condensed summary of the amount of lead found before and after washing on the four varieties in Plots 1 to 6. The spray treatments on this series of plots are shown elsewhere. None of them could be considered as heavy lead arsenate treatments. In four out of the six plots, calcium arsenate was substituted for lead arsenate in the last application. It was not to be expected that the wide variations which were found between high and low samples in 1935 would be found in this comparatively light spray treatment. However, an examination of the results of analyses made on samples of Jonathan, Delicious, and Stayman from Plot 9 which received seven applications of lead arsenate in addition to the petal-fall spray does not indicate as great differences between varieties as in the work of 1935.

TABLE 20.—Range of Residue on Four Varieties under Same Spray Treatments, 1936

(Lead residue, grain per lb. of fruit)

Variety	Before washing			After washing		
	Highest residue	Lowest residue	Average residue	Highest residue	Lowest residue	Average residue
McIntosh .....	0.028	0.008	0.015	0.006	0.004	0.005
Grimes .....	0.040	0.009	0.020	0.006	0.003	0.005
Jonathan .....	0.032	0.007	0.017	0.006	0.005	0.006
Stayman .....	0.029	0.010	0.017	0.006	0.004	0.005

From Table 20 it will be noted that the lead on the Grimes exceeded that on the other three varieties on the unwashed samples. There was, however, no appreciable difference among the washed samples. The finish of all the varieties in 1936 was uniformly good; whereas Jonathan had been considerably russeted in 1935. In 1936 the Grimes samples used for analyses were somewhat smaller in size than it was possible to obtain of the other varieties. From the experience of these two seasons it may be concluded that size of fruit is the most consistent cause of differences but that russetting of the skin may in some seasons be an important factor in building up the residue and increasing the difficulty of removing it.

It should be stated in connection with the data presented in Table 20 that the washing was done within a day or two after the apples were picked.

## TYPES OF WASHERS COMPARED

Two types of washers were used in 1936: (a) an under brush flood type (Fig. 4) and (b) a homemade flotation washer (Fig. 5). In the under brush flood washer used in this work the apples pass over a series of brushes while being subjected to the acid bath by means of a splash system. From the acid bath the apples pass into the rinse compartment where they are subjected to a splash system and a spray of clear rinse water from above; then they pass over a series of drying rolls to the grading table. In the flotation washer the apples are compelled by means of wood paddles attached to an endless chain belt to float through an acid bath, into a bath of rinse water, and finally onto the grading table.

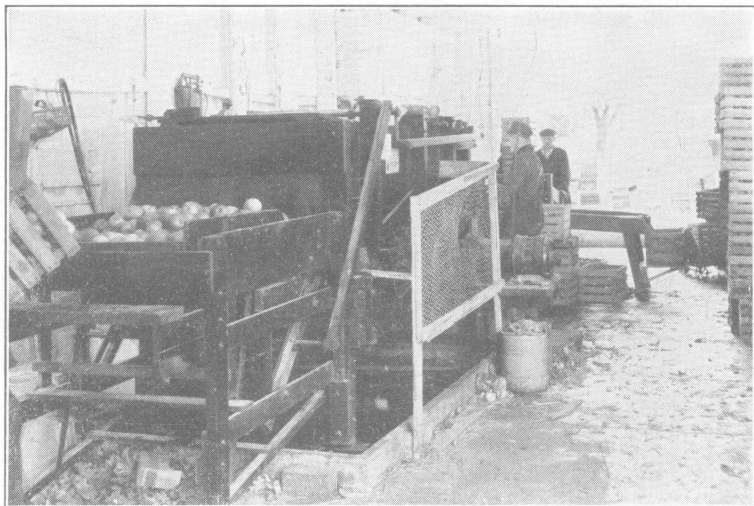


Fig. 4.—An under brush flood type of washer

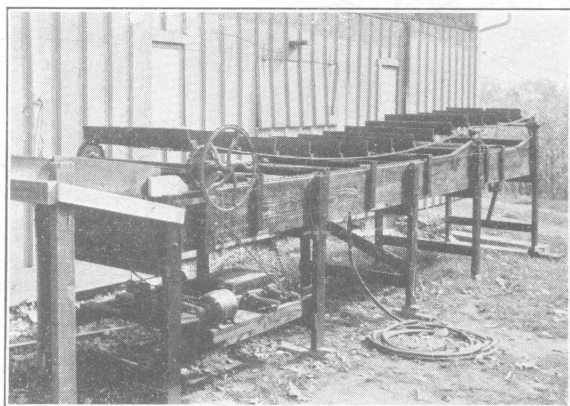


Fig. 5.—Homemade flotation washer

The flotation washer was not available early enough in the year to make it possible to compare its efficiency with that of the under brush flood type on all varieties. However, samples of Stayman from nearly all the plots, as well as a number of samples of several other varieties, were washed in the flotation washer. Some of the results secured on samples from several of the spray plots are shown in Table 21. It will be noted that the average lead residue for all of the unwashed fruit included in these data was 0.044. The average for the samples washed in the under brush flood type of washer was 0.007 and for the flotation washer, 0.013. The under brush flood type of washer removed an average of 84.1 per cent of the residue and the flotation washer, an average of 70.5 per cent. These results compare with the 86 per cent removal in the under brush flood type and the 81 per cent in the flotation type reported by



Hough (12). The flotation washer used by Hough differed considerably in construction from the type used at Wooster. Frear and Worthley (8) reported 71.4 per cent removal of lead by means of a flotation washer. The flotation washer used by these workers in Pennsylvania was very similar in construction to the one used in the work reported in this bulletin.

TABLE 21.—Efficiency of Under Brush Flood Washer Compared with Homemade Flotation Type, 1936

Spray plot	Variety	Washing treatment		Lead residue per lb. of fruit
		Strength of acid solution	Type of washer	
		<i>Pct.</i>		<i>Gr.</i>
9	Jonathan.....	.....	Not washed	0.071
9	Jonathan.....	1	Under brush flood	.008
9	Jonathan.....	1	Flotation	.026
3	Stayman.....	.....	Not washed	.024
3	Stayman.....	1	Under brush flood	.008
3	Stayman.....	1	Flotation	.010
4	Stayman.....	.....	Not washed	.015
4	Stayman.....	1	Under brush flood	.004
4	Stayman.....	1	Flotation	.007
5	Stayman.....	.....	Not washed	.017
5	Stayman.....	1	Under brush flood	.007
5	Stayman.....	1	Flotation	.013
6	Stayman.....	.....	Not washed	.029
6	Stayman.....	1	Under brush flood	.006
6	Stayman.....	1	Flotation	.013
9	Stayman.....	.....	Not washed	.075
9	Stayman.....	1	Under brush flood	.010
9	Stayman.....	1	Flotation	.009
9	Stayman.....	1½	Under brush flood	.012
9	Stayman.....	1½	Flotation	.012
10	Stayman.....	.....	Not washed	.030
10	Stayman.....	1	Under brush flood	.009
10	Stayman.....	1	Flotation	.015
10	Stayman.....	1½	Under brush flood	.006
10	Stayman.....	1½	Flotation	.009
15	Stayman.....	.....	Not washed	.020
15	Stayman.....	1	Under brush flood	.005
15	Stayman.....	1	Flotation	.006
9	Delicious.....	.....	Not washed	.115
9	Delicious.....	1	Under brush flood	.006
9	Delicious.....	1	Flotation	.018
13	Baldwin.....	.....	Not washed	.022
13	Baldwin.....	1	Under brush flood	.003
13	Baldwin.....	1	Flotation	.009
14	Baldwin.....	.....	Not washed	.045
14	Baldwin.....	1	Under brush flood	.006
14	Baldwin.....	1	Flotation	.016
Av.	.....	.....	Not washed	.044
Av.	.....	.....	Under brush flood	.007
Av.	.....	.....	Flotation	.013
Av. per cent removed by under brush flood, 84.1				
Av. per cent removed by flotation, 70.5				

In the 1935 work at Wooster the percentage of lead removed by the under brush flood type washer ranged from 73 to 95 per cent. However, it should be noted that in 1935 the acid solution was heated to 85° or 90° F.; whereas the samples from the 1936 work included in Table 21 were washed in cold solution

in both the under brush flood and flotation washers. The results of washing reported elsewhere in this bulletin show very conclusively that heating increases the efficiency of the solution. It was not convenient to arrange a heating device for the flotation washer in 1936 and the data presented in Table 21 are, therefore, confined to samples washed in solutions of comparable temperatures in the two machines. The percentage of lead removed from the samples washed with the under brush flood type is probably less than it would have been in a heated solution. It is also likely that heating the solution would have increased the efficiency of the flotation washer.

### BRUSHING COMPARED WITH WASHING

In 1936 as in 1935 dry cleaning with a mechanical brush or wiper was compared with washing. The results of this comparison are shown in Table 22. The data presented are typical of a considerable number of samples analyzed for lead residue. The highest percentage of lead removed from any of this group of samples by brushing was 35.6 per cent. In one case the brushed sample actually had a larger deposit of lead residue than the unwashed sample from the same plot. The percentage of lead removed by the under brush flood washer using a 1 per cent acid solution at hydrant temperature ranged from 66.7 per cent to 86.7 per cent, and the samples washed in a like strength of acid in the flotation washer, from 50 per cent to 88 per cent. The brush was also used as a supplement to washing in both the under brush flood and flotation washers. The samples which were washed and then wiped were in every case well below the tolerance before they were wiped. In no case of the dozen or more samples analyzed did brushing following washing appreciably reduce the lead residue. With the lead tolerance at 0.018, the mechanical brush was not satisfactory as a cleaning device if the untreated samples had a lead residue much above 0.020. Moreover, it is entirely possible that brushing may even add to the lead residue, as was true in one instance in the analyses shown in Table 22. The cloths used in the mechanical brush require frequent changing where the lead residue is likely to be above the tolerance. It has been shown (11) that a large part of the residue on an apple is confined within the depressions around the stem and calyx. This accounts in part for the inefficiency of the wiper in cleaning apples if the residue deposit is very much above the tolerance. Streeter et al (16) have shown that 39 per cent of the total residue on nine varieties was contained within the cavity and basin of the apples. Eight of the nine varieties used in this work were medium to large-size varieties.

TABLE 22.—Brushing Compared with Washing, 1936  
(Grain of lead per pound of fruit)

Spray plot	Variety	Lead residue before treatment	Lead residue after brushing	Per cent of lead removed by brushing	Lead residue after washing, under brush flood	Per cent of residue removed by under brush flood	Lead residue after washing, flotation	Per cent of residue removed by flotation
3	Grimes ...	0.029	0.020	31.0	0.006	79.3	.....	.....
6	Grimes ...	.040	.036	10.0	.006	85.0	.....	.....
3	Jonathan..	.028	.020	28.5	.006	78.6	.....	.....
6	Jonathan..	.032	.027	15.6	.006	81.3	.....	.....
3	Stayman..	.024	.030	+25.0	.008	66.7	0.010	58.3
6	Stayman..	.029	.029	0.0	.006	79.3	.013	55.2
9	Stayman..	.075	.060	20.0	.010	86.7	.009	88.0
10	Stayman..	.030	.028	6.7	.009	70.0	.015	50.0
13	Baldwin..	.022	.019	13.6	.003	86.4	.009	59.1
14	Baldwin..	.045	.029	35.6	.006	86.7	.016	64.4

The record of these 2 years of work at Wooster, as well as the experience of growers elsewhere in the State (14), shows conclusively that the mechanical brush cannot be relied upon to remove residue from apples at or above the present tolerances.

The mechanical brush is, no doubt, useful for cleaning dirty apples and may have some value as a means of polishing and drying the apples from the flotation washer. Mechanical brushes which are equipped with blower attachments are more effective in removing residue than those not so equipped.

#### VALUE OF WETTING AGENT IN WASH SOLUTION

Vatsol was used as a wetting agent in the 1935 washing experiments and in part of the work in 1936. In both years this material was used at the rate of 5 pounds per 100 gallons of washing solution. When vatsol is added to the solution it is necessary to add a defoaming agent to prevent excessive foaming; for this purpose an oillike material known as anti-foam was used at the rate of 6 to 8 pints per 100 gallons of solution.

The data presented in Table 23 would seem to indicate that under the conditions existing in these particular experiments the addition of vatsol was not justified. The layout of the work in 1936 was not designed to give as complete information on this feature as might be desired.

TABLE 23.—Influence of Wetting Agent on Efficiency of Wash Solution, 1936

Spray plot	Washing treatment	Lead residue per pound of fruit				
		Variety				
		McIntosh	Grimes	Jonathan	Stayman	Delicious
3	Not washed .....	0.022	0.029	0.028	...	.....
	1% acid, cold .....	.005	.006	.006	...	.....
	1% acid, cold, plus vatsol.....	.006	.005	.005	.....	.....
6	Not washed .....	.028	.040	.032	.. ..	.....
	1% acid, cold .....	.006	.006	.007	.. ..	.....
	1% acid, cold, plus vatsol .....	.007	.007	.007	.....	.....
9	Not washed .....	.....	.....	.071	0.075	0.115
	1½% acid, cold .....	.....	.....	.009	.012	.008
	1½% acid, cold, plus vatsol .....	.....	.....	.009	.008	.006
	1½% acid plus vatsol, heated to 85°-90° F.....	.....	.....	.008	.006	.005
10	Not washed .....	.....	.....	.....	.030	.020
	1½% acid, cold .....	.....	.....	.....	.....	.005
	1½% acid plus vatsol, cold .....	.....	.....	.....	.006	.003
	1½% acid plus vatsol, heated...	.....	.....	.....	.005	.004

It will be noted, however, that the addition of vatsol to the hydrant-temperature washing solution had practically no influence on the effectiveness of the washing solution. Heating the solution containing vatsol seemed to increase the efficiency slightly as compared with the unheated solution either with or without vatsol. It may be well to emphasize that none of the spray plots in the residue work were sprayed late in the summer with mineral oils. Under such conditions a wetting agent may be justified. The results of this limited observation on the value of the wetting agent are in harmony with the work of Frear and Worthley (7) in Pennsylvania. Hough (12) in Virginia found that wetting agents added little to the efficiency of cold solutions but

that heating the solution invariably increased the efficiency of the solution and, as a rule, was sufficient to clean the fruit within the tolerance without the aid of a wetting agent. This worker found that where considerable oil had been included in the spray program the addition of a wetting agent to the heated acid solution was necessary. Burkholder and Ford (2) found that when washing was delayed late into the winter season, the wetting agent used in a cold washing solution added nothing to its efficiency.

#### *SODIUM SILICATE COMBINED WITH SPRAY PROGRAM*

An effort was made in 1936 to investigate the possibility of using sodium silicate sprayed on the trees as a means of removing the lead residue. On one plot of trees containing Baldwin and Stayman the ordinary commercial sodium silicate was applied in connection with the last lead arsenate spray, July 28, at the rate of 1 gallon per 60 gallons of solution. Within a few days much of the foliage on the Baldwin trees began to show burning, and within the next 2 weeks many of the leaves had fallen. The Stayman trees showed little burning. However, this experience with Baldwin indicates that sodium silicate cannot be safely recommended for use, particularly at that season of the year. In order to prevent further injury the trees were drenched with water and lime as soon as the extent of the damage became apparent. The subsequent spray treatment of this plot made it impossible to secure any information on the effectiveness of sodium silicate used in the last codling moth spray in removing residue. The fruit from both Baldwin and Stayman in this plot shriveled badly in storage.

In another plot the Baldwin and Stayman trees were sprayed with sodium silicate at the same strength indicated above 1 week before they were picked. The trees were rinsed with clear water as soon as they were sprayed. No injury to the foliage was noted following this spraying.

From the results shown in Table 18 it will be seen that the application of sodium silicate, together with the accompanying rinsing with the sprayer, did reduce the lead residue but not under the tolerance. In the case of Baldwin, the analyses showed a lead residue of 0.034 before, and 0.022 after applying the sodium silicate. This compared with 0.038 and 0.028 on the Stayman. The results of 1936 do not offer much promise that this method of removing residue will be effective or practical.

#### **LEAD AND ARSENIC REMOVAL COMPARED**

The major emphasis in the work reported in this bulletin has been on the removal of lead rather than arsenic. At the time this work was started enforcement agencies were directing particular attention toward lead removal. Also, it had previously been shown (7, 15) that the proportion of lead and arsenic residue as the result of spraying with lead arsenate was slightly more than 2 times as much lead as arsenic ( $\text{As}_2\text{O}_3$ ). Since this work was inaugurated in 1935 Hough (12) has published results of analyses made in Virginia which confirm the earlier reports of the ratio of lead and arsenic residues.

With the tolerance of lead at 0.018 and that of arsenic at 0.01, it was felt that any cleansing operation which would reduce the lead below the tolerance would also be satisfactory for removing the arsenic. This is borne out by the results shown in Table 24. From this table it will be noted that washing reduced the lead and arsenic residues to well within the respective tolerances

in every case. The highest percentages of residues removed were on the plots which had relatively heavy residue loads before washing. This was to be expected because the amounts of residue on the average washed samples tend to be relatively uniform; whereas there is frequently wide variation on the unwashed samples, even from plots similarly sprayed.

TABLE 24.—Lead and Arsenic Residues Compared. Variety Stayman, 1936  
(All plots sprayed with lead arsenate in petal fall)

Spray program	Washing treatment	Grain of lead per lb. of fruit	Per cent of lead removed	Grain of arsenic, $As_2O_3$ , per lb. of fruit	Per cent of arsenic, $As_2O_3$ , removed
Lead arsenate plus oil, 1st cover Calcium arsenate, last cover	Not washed Under brush flood, 1% acid	0.010 .006	..... 40.0	0.006 .004	..... 33.3
Lead arsenate, 1st cover Lead arsenate, last cover	Not washed Under brush flood, 1% acid	.024 .008	..... 66.7	.010 .005	..... 50.0
Lead arsenate, 1st cover Lead arsenate, 2nd cover Calcium arsenate, last cover	Not washed Under brush flood, 1% acid	.015 .004	..... 73.3	.009 .003	..... 66.7
Lead arsenate plus oil, 1st cover Lead arsenate, 2nd cover Lead arsenate, last cover	Not washed Under brush flood, 1% acid	.029 .006	..... 79.3	.012 .005	..... 58.3
Lead arsenate, 1st cover Lead arsenate, 2nd cover Lead arsenate, 3rd cover Calcium arsenate, last cover	Not washed Under brush flood, 1% acid	.020 .006	..... 70.0	.031 .004	..... 87.1
Lead arsenate, 1st cover Lead arsenate, 2nd cover Zinc arsenate, last cover	Not washed Under brush flood, 1% acid	.012 .007	..... 41.7	.026 .005	..... 80.8
Lead arsenate plus oil, 1st cover Lead arsenate plus oil, 2nd cover Lead arsenate, 3rd cover Lead arsenate, 4th cover Lead arsenate, 5th cover Lead arsenate, 6th cover Lead arsenate, 7th cover	Not washed Under brush flood, 1% acid	.075 .009	..... 88.0	.031 .005	..... 83.9
Lead arsenate plus oil, 1st cover Lead arsenate, 2nd cover Lead arsenate, 3rd cover Lead arsenate, 4th cover Calcium arsenate, 5th cover Calcium arsenate, 6th cover Calcium arsenate, 7th cover	Not washed Under brush flood, 1% acid	.030 .009	..... 70.0	.032 .006	..... 81.3
Lead arsenate, 1st cover Lead arsenate, 2nd cover Lead arsenate, last cover Sprayed with sodium silicate 1 week before picking	Not washed Under brush flood, 1% acid	.028 .006	..... 78.6	.008 .003	..... 62.5

The results shown in Table 24 seem to indicate that washing is about equally effective in removing lead and arsenic, particularly when the difference in the present tolerances is considered.

No analyses for fluorine were made in connection with the residue projects at Wooster either in 1935 or 1936. None of the plots included in the layout were sprayed with any of the so-called fluorine sprays in any of the summer applications. Hough of Virginia (12) has shown that the acid solution used in removing lead and arsenic was satisfactory for removing fluorine but that in case of heavy deposits of fluorine residue the heated solution was considerably more effective than unheated acid.

Groves and others (9) of Washington have recently published the results of experimental work on the removal of fluorine. The results of a single year's experience would indicate that where the deposits are heavy following the use of fluorine compounds the residue is more difficult to remove than a like amount of lead or arsenic.

### INFLUENCE OF WASHING ON STORAGE QUALITIES

The plan of the residue experimental work in 1935 and 1936 did not contemplate very elaborate observations on the influence of washing on keeping qualities. In 1935, however, samples of washed and unwashed Grimes and Jonathan were packed in crates and placed in cold storage. On January 16, 1936, these apples were examined. There was no indication that any of the apples had been affected by the acid bath. All of the apples did show more or less shriveling. The results of the examination to determine the extent of the shriveling are shown in Table 25.

TABLE 25.—Influence of Washing on Keeping Quality

Variety	Treatment	Total no. of apples	No. of apples shriveled	Per cent of apples shriveled
Jonathan.....	Not washed	148	41	28
Jonathan.....	Washed	148	22	15
Grimes.....	Not washed	100	28	28
Grimes.....	Washed	108	3	3

It should be stated that the unwashed samples were from plots which were rather heavily covered with residue containing a large amount of lime. It is likely that the lime had a dehydrating effect on the unwashed samples. Like observations were also extended to Baldwin in common storage with results very similar to those indicated in Table 25.

Marshall, Overley, and Groves (13) found that all the washing treatments included in their investigations on the loss of moisture subsequent to washing accelerated the rate of loss. The rates of moisture loss from ordinary washing were not of serious proportions. The addition of mineral oil to the washing solution increased the rate of moisture loss. Diehl et al (3) found that acid burning of the fruit was largely due to insufficient rinsing or to careless washing methods. Varieties most seriously affected were those with open calyx tubes. These workers have also pointed out that arsenical injury may be easily mistaken for acid burning. Acid injury may occur on any part of the apple; whereas arsenical burn is generally confined to the calyx end of the apple and is somewhat darker in color. Streeter et al (16) have reported that washing apples in New York did not materially affect their keeping quality. Frear and Worthley (8) from Pennsylvania state that "washing with dilute solutions of

hydrochloric acid at concentrations of 2 per cent or less apparently did not impair the keeping qualities of marketable apples when properly rinsed. Packing the apples when wet did not affect their keeping qualities in storage. Cull apples, however, in which there were a number of cut and bruised fruits did not keep well after washing, apparently because of the entrance of the acid into the flesh of the fruit. The solution apparently was very difficult to remove by rinsing and exerted a harmful effect later".

The data presented above and the citations referred to indicate that washing, if properly done, will not materially affect the keeping qualities. These conclusions, however, refer to the action of the washing solution on the apples and do not take into consideration mechanical injuries which may result from bruising or the exposure to overheated washing solutions during the operations. Every effort possible should be made to eliminate bruising, and it is best to keep the washing solution under 110° F.

#### LEAD FOUND ON UNSPRAYED APPLES

In 1936 a few samples of apples were taken from a small area of the Station orchards which had received no spray treatment following the dormant period. The analyses made of Stayman from this unsprayed plot showed a residue of 0.002 lead.

The analyses for lead on the samples from Plots 7 and 8, which were sprayed throughout the season of 1936 with calcium arsenate, frequently showed a trace of lead on both unwashed and washed fruit. One unwashed sample of Stayman taken from Plot 8 had a residue of 0.003. Generally, however, the lead residue from these plots was 0.002 or less.

No effort was made to establish the source of the very small amount of lead on these unsprayed or calcium arsenate-sprayed plots. The same sprayer which was used in applying lead arsenate to other plots was used in spraying the calcium arsenate plots. It may be that enough lead adhered to the tank to make a slight deposit on the apples. The unsprayed trees were 60 feet or more from the nearest sprayed tree; however, it is not impossible that the material may have drifted that distance. It should be noted that these unsprayed trees were so seriously affected by disease and insects that they lost their foliage prematurely and that the fruit was 100 per cent culls. In the case of the washed samples small quantities of lead may have been added to the apples in the process of washing. The samples of wiped apples from Plots 7 and 8 in several cases showed an appreciable increase of lead as compared with the unwashed samples. In such cases it seems likely that the process of wiping with the mechanical brush actually added lead to the apples from the lead-contaminated cloths.

#### RESIDUE ON FRUIT AT BEGINNING OF SECOND-BROOD SPRAYING, 1936

A number of analyses of the immature apples were made at the time the first of the second-brood codling moth sprays was made (July 29) to determine the amount of lead then remaining on the fruit. These samples were placed in cold storage, and the analyses were made at the same time the mature fruit was analyzed.

In Table 26 are presented the results of analyses of samples from four representative plots which were sprayed with lead arsenate before the first spray for the second brood; some substitute for lead arsenate was used in the latter spray. The lead residue on these four plots at the time the July 29 application was made ranged from 0.032 on Plot 12 up to 0.052 on Plot 11, which had received three early summer applications in addition to the petal-fall spray. It would appear that the adhesive properties of the summer oil used in the June 3 application on Plot 2 had tended to retain a greater amount of residue on that plot than was retained on the adjacent plot (Plot 1) where no oil had been added to the lead arsenate. It will also be noted that at harvest time the lead residue was under the tolerance on all of these plots except Plot 11.

TABLE 26.—Lead Residue on Stayman from the Use of Lead Arsenate for First-brood Codling Moth Sprays, 1936

Plot	Spray treatment	Residue, July 30, grain of lead per lb. of fruit	Residue at harvest, grain of lead per lb. of fruit
1	L A, June 3 C A, July 29	0.035	0.010
2	L A plus oil, June 3 C A, July 29	0.044	0.010
11	L A, June 3 L A, June 17 L A, July 1 C A, July 29	0.052	0.020
12	L A, June 3 L A, June 17 Z A, July 29	0.032	0.012

It should be remembered that the increase in size of apples is one of the main factors in reducing the amount of residue from late July until picking time.

#### TANDEM WASHING

In sections where the problem of residue removal is particularly serious the use of tandem washers has been necessary. Under some conditions tandem washing involves the use of both an alkaline and an acid wash solution. Another tandem arrangement sometimes employed utilizes two washers connected with each other using like wash solutions. It does not seem likely that tandem washers will be necessary in Ohio.

In 1936 several samples of apples were first washed in the flotation washer and then run through the under brush flood type of washer. The results from a plot the unwashed fruit of which had a relatively high residue load are shown in Table 27.



TABLE 27.—Tandem Washing, 1936  
Variety Stayman

Spray plot	Washing treatment	Grain of lead per lb. of fruit
9	Not washed .....	0.075
	Under brush flood—1% acid.....	.010
	Flotation—1% acid.....	.009
	Flotation—1% acid plus under brush flood—1% acid.....	.007
	Under brush flood—1½% acid.....	.012
	Flotation—1½% acid.....	.012
	Flotation—1½% acid plus under brush flood—1½% acid.....	.006

It will be noted that the double washing did reduce the lead as compared with a single washing through one machine but that the residue was well within the tolerance after a single washing.

#### HYDROCHLORIC ACID USED IN WASHING APPLES

The commercial grade of hydrochloric (muriatic) acid was used to prepare the wash solution. This acid is obtained in glass carboys containing approximately 12 gallons. The strength of the acid in degrees Baumé is indicated on the outside of the wood frame used for shipping the carboy. The acid used in the work reported in this bulletin was 18° Baumé. Eighteen-degree muriatic acid is 27.92 per cent hydrochloric acid. A dilution table for acid of this strength is presented elsewhere in this bulletin. The acid is also frequently obtained with a density of 20° Baumé, 31.45 per cent acid.

#### HANDLING THE ACID

In transferring the acid from the carboy to the washing machine workmen should be cautioned to use extreme care not to spill any of the acid on their person or clothes. Even at relatively dilute strengths the acid is caustic to the flesh and corrosive to metal which has not been acidproofed. So far as possible, all metal parts of the washer which are exposed to the acid should be covered with an acid-resisting paint. The acid also reacts against lime, and cement floors near the washer should be covered with heavy oil or paint. When the solution is drained from the acid compartment it is a good plan to add large quantities of water if it is to be emptied into a sewer, in order to prevent damage to the cemented joints of sewer tile. The waste acid should not be emptied so that it will come in contact with growing plants or trees. Containers of all kinds used in handling the acid should be wood, porcelain lined, earthenware, or glass. An acid pump or a tilting device to facilitate the withdrawal of the acid from the carboy is another means of guarding against possible injury to workmen.

In commercial practice the acid compartments of washing machines are not generally drained more often than once for 1000 bushels of fruit, and sometimes even a greater quantity is washed before a fresh acid solution is added. However, it is occasionally necessary to add small amounts of acid to the washing solution to restore it to the required strength. In doing this probably the best method is to add enough water to bring the solution to the designated level in the acid compartment, make a test to determine the strength of the solution, and then add the required amount of acid.

A stock solution diluted to the right strength may be prepared in a wood barrel and used as a source from which to replace a depleted supply of solution in the acid compartment of the washer. The stock solution plan is better adapted for use where the required strength is not in excess of 1 per cent acid. For practical purposes a variation of from  $\frac{3}{4}$  to  $1\frac{1}{2}$  per cent acid may be tolerated under most conditions in Ohio.

TABLE 28.—Rate of Acid Dilution per 100 Gallons of Solution

Strength of solution	18° Baumé muriatic acid, quarts required for 100 gallons of washing solution (approximate)	20° Baumé muriatic acid, quarts required for 100 gallons of washing solution (approximate)
1 per cent solution.....	14	12½
1½ per cent solution.....	22	19
2 per cent solution.....	29	25

#### LENGTH OF EXPOSURE TO ACID BATH

In the under brush flood type washer used in the experimental washing in 1935 and 1936 it required from 30 to 45 seconds for the apples to pass through the acid bath. It required a somewhat shorter period for the apples to pass through the rinse water. In the flotation washer used in 1936, 3 minutes were required for the apples to pass through the acid bath and the apples were in the rinse water compartment 1 minute. No attempt was made to measure the influence of using the washers at varying speeds or different quantities of rinse water. It has been shown, however, (12) that the amount of rinse water required per bushel depends upon the strength of the acid solution. It has also been demonstrated (12) that where a relatively strong wash solution is being used the acid carried over into the rinse compartment, especially on flotation washers, is likely to make the rinse water quite acid. Under such conditions the addition of small amounts of lime to the rinse water is necessary to neutralize it. In the under brush flood type of washer used at the Station, the rinse water compartment was connected by hose with the water system, and approximately 3 gallons of water per bushel of fruit were consumed. The overflow was open constantly and the water drained out at the same rate it entered the rinse compartment. Less water was used in the flotation washer than in the under brush flood type. An abundance of clean rinse water is an essential requirement of any washing program, regardless of the type of washing equipment.

#### METHOD OF TESTING WASH SOLUTION

The strength of the acid wash solution gradually diminishes while the apples are being washed. This is due to the neutralization of the acid by the residue and the natural dilution by moisture on the fruit. There is also some slight loss of volume in the constant carry-over into the rinsing compartment. It is necessary to test the strength of the solution occasionally to make sure that the strength of the acid does not fall below the required standard.

The method used at this Station in testing the strength of the acid was a comparatively simple process and is briefly described here. Workers at other Stations have used methods slightly different which are as satisfactory as the

process described. Haller, Smith, and Ryall (10), in Farmers' Bulletin 1752 of the United States Department of Agriculture describe in detail a method using slightly different materials but essentially the same as the one given below.

The grower may safely adopt either of these methods. The supplies required can be obtained through a local drug store or chemical supply firm. For convenience, the dilutions given in Table 29 are approximate but are accurate enough for practical purposes. It is, of course, not possible to keep the strength of the acid solution exact at all times. It requires approximately  $3\frac{1}{2}$  gallons of 18° Baumé (27.92 per cent) muriatic acid in 100 gallons of solution to make 1 per cent acid (by weight). Approximately 3 gallons and 1 pint of 20° Baumé (31.45 per cent) are required to make a 1 per cent solution.

TABLE 29.—Quantity of Acid Required to Make Desired Strength of Wash Solution

Number of cc. of $\frac{1}{2}$ normal sodium hydroxide required to neutralize 5 cc. of solution from washer	Strength of acid by weight in washer is as indicated below	Pints of 28% acid required to add to 100 gal. in washer to bring test to 1% by weight	Pints of 28% acid required to add to 100 gal. in washer to bring test to $1\frac{1}{2}$ % by weight
	<i>Pct.</i>		
2.0	0.73	7.7	22.0
2.1	0.77	6.7	20.9
2.2	0.80	5.7	20.0
2.3	0.84	4.6	18.9
2.4	0.88	3.4	17.8
2.5	0.91	2.6	16.9
2.6	0.95	1.4	15.8
2.7	0.98	0.6	14.9
2.8	1.02	.....	13.8
2.9	1.06	.....	12.6
3.0	1.09	.....	11.8
3.1	1.13	.....	10.6
3.2	1.17	.....	9.4
3.3	1.20	.....	8.6
3.4	1.24	.....	7.4
3.5	1.28	.....	6.3
3.6	1.31	.....	5.4
3.7	1.35	.....	4.3
3.8	1.39	.....	3.2
3.9	1.42	.....	2.3
4.0	1.46	.....	1.2
4.1	1.49	.....	0.3

DIRECTIONS FOR MAKING TEST OF STRENGTH OF ACID  
IN WASHING MACHINE

Equipment necessary:

- One pint of  $\frac{1}{2}$  normal sodium hydroxide
- One 5-cc. pipette (use for acid only)
- One 10-cc. pipette graduated from 1 to 10 (use for sodium hydroxide only)
- One 2-oz. bottle of phenolphthalein indicator
- One 3- or 4-oz. bottle

Making the test:

1. Take cup or bottle of liquid from acid compartment.
2. Take 5 cc. of washing liquid from cup and put in bottle; add 2 drops of phenolphthalein indicator.

3. Take 10 cc. of  $\frac{1}{2}$  normal sodium hydroxide from supply bottle and add to the 5 cc. of wash solution drop by drop until the wash solution turns red.
4. Read the number of cc. of sodium hydroxide required to neutralize the 5 cc. of washing acid. (Pour remainder of sodium hydroxide back into bottle).
5. Check up on strength of acid solution every 2 hours when running washer to capacity. Many failures to remove residues to below tolerance are caused by allowing the acid solution to become too weak.
6. See chart on following sheet for strength of acid indicated by each titration.

### FLOTATION WASHERS

In the design and construction of a flotation type washer there are several factors which must be given thorough consideration:

1. Effectiveness of machine in removing spray residues
2. Low cost, both in construction and operation
3. Use of acid-resistant materials in the construction of the washer
4. Simplicity of design
5. Capacity sufficient to handle a year's crop
6. Prevention of injury to fruit by bruising or crushing

In most tests conducted to date the flotation washer has not been as effective as the brush type. This is to be expected because of the abrasive action of the brushes on the fruit and because rotating the apples exposes the complete surface to the brush action. In this way the calyx and stem ends of the apples are usually well cleaned.

A flotation washer generally consists of a large tank divided into two sections. One section contains an acid solution to remove the spray residue and the other contains water for rinsing purposes. The apples are supplied to the machine through a hopper placed at the end of the acid tank. They are moved forward through both solutions by means of conveyors of various types. The effectiveness of this type of washer, therefore, depends a great deal upon the time the fruit remains in the acid and rinse sections, together with the revolving action which the apples receive as they are moved forward. A more effective job will be done if the apples are washed soon after picking, for when apples are placed in storage for a time the spray residue becomes embedded in the waxy coatings of the apples and is hard to remove. Heating the acid solution helps greatly in removing or dissolving the spray residues but, of course, adds to the complication and cost of the machine. If at all possible, a spray of water should be used to aid in the rinsing of the fruit.

Wood is the material generally recommended for the construction of a flotation type apple washer. It is easy to obtain, is fairly resistant to the action of acids, and, with the services of one skilled in the use of woodworking tools, can be worked into a practical machine of low cost. It has its disadvantages, however, of contraction in dry weather and overexpansion in contact with moisture. Also, it is sometimes difficult to secure material free of knots and evidence of warp.

Simplicity of design will influence the cost of both construction and operation. A complicated design will add to the cost of building the unit and possibly result in an increase in the size of power unit required to operate it. A simple design will tend to lessen the danger of damage to the fruit and will avoid repairs over short periods of time. Any elaborate detail in the construction of the washer should be avoided unless such features add greatly to the efficiency of operation.

The length of the acid and rinse sections of the washer should be more or less standard; the widths may vary to meet the desired capacity. For all practical purposes, lengths of 14 feet for the acid section and 6 feet for the rinse section have been found sufficient. From tests made to date, 5 minutes or less, depending on the amount of residue on the apples, are sufficient to dissolve the spray residue. This length of tank, therefore, will offer sufficient time and yet not limit the capacity beyond a practical point. The depth of the tanks need not be over 10 inches. Unless the washer is to be located more or less permanently, it is advisable to construct the two sections as separate units in such a way that they can be bolted together for operation. If made this way, they can be detached for convenience in transporting, and this offers a means of preventing the acid solution from seeping into the rinse tank and vice versa.

The two tanks should be constructed from 2-inch lumber of widths specified to meet the width and depth of the tanks, with little or no waste of lumber. A No. 1 grade of well-seasoned yellow pine is very satisfactory, providing it is free of knots and is not warped. All adjacent edges of the boards must be "jointed" so that they will fit together tightly. Before these edges are placed together, some elastic sealing compound, such as an asphalt roofing cement, should be applied between them to insure against leaks.

Steel tie rods are very satisfactory for clamping and holding the boards together to form the tank. However, they must be placed in such positions that they will not contact the acid solution, as acid will attack steel readily. Lag screws can be used where it is impossible to use tie rods. This sort of construction will make it possible to tighten the tank should leaks develop.

A coating of acid-resisting paint may be applied to the inside of both tanks although this is not entirely necessary. All bolt and nail heads must be countersunk and a coating of wax must be placed over them to prevent contact with the acid solution.

Various means have been devised to move the fruit through the acid and rinse sections. However, other devices must be installed to aid in turning the apples so that the complete surface may be exposed to the acid solution. Cotton drapers, inclined raised bottoms, and paddle wheels have given very good results. Where apples are moved up an incline and out of the liquid a glass surface should be installed; this will eliminate much friction and prevent bruising to a great extent. All conveying equipment of steel should be painted with an acid-resistant paint.

As the conveyor travels at a very low rate of speed, reduction can be made by means of combinations of various sized sprockets, by worm-and-worm gears, or by a regular speed reduction unit. In order to prevent bruising or other injury to the fruit, the sides of the tanks at the water line and the sides and bottoms of the hoppers should be lined with sponge rubber of about  $\frac{3}{8}$ -inch thickness.

Machines of the flotation type are relatively inexpensive and fairly efficient for the small grower. They can be built by anyone who is skillful with wood-working tools. However, if one is not mechanically inclined, he should not

attempt to construct one. In such cases it will be advisable to purchase a machine directly from a commercial manufacturer, as the inefficiency which may result from a poorly constructed outfit will cost more than the price of the commercially manufactured machine.

### PRACTICAL CONSIDERATIONS

It is not the province of this bulletin to suggest the necessity of washing apples, but merely to indicate, as nearly as possible, the amount of residue which will result from given spray programs and practical means of removing it. To this end, the following practical considerations may be emphasized in connection with any program that contemplates the installation of fruit washers in Ohio:

1. The mechanical brush or wiper is not adequate for the removal of spray residues in Ohio.
2. One of the first requirements for the installation of fruit washers is that there be available at harvest time an adequate supply of clean water. Plans should be made to supply not less than 3 gallons of water for each bushel of fruit to be washed.
3. The appearance of washed fruit properly dried is superior to that of unwashed fruit and equal to that of brushed fruit.
4. Some method of drying is essential. The absorbent rolls system of the under brush flood type of washer used in the experimental work reported here was satisfactory. Flotation washers should be equipped with some type of drier. A mist type rinsing system is also advisable for the flotation washer.
5. Plans for new packing sheds may well allow space for the additional room required for washing equipment.
6. The construction of a flotation washer requires considerable mechanical skill and the availability of a good set of woodworking and metal tools.
7. Apple growers having a production of 1000 bushels or less who desire to wash their fruit will probably find dipping tanks more economical than washing machines. Methods of constructing and using homemade dipping tanks have been described by workers of the United States Department of Agriculture (10) and the Virginia Experiment Station (11). Provision should be made for rinsing the apples after they have been dipped in the acid bath. Where the residue is likely to be relatively heavy, the dipping method may not be adequate.
8. Growers should consult spray authorities before making radical departures from proved spray programs in order to avoid excessive residues.

## SUMMARY

The results of the 2 years' (1935-1936) experimental apple washing at the Ohio Station may be summarized as follows:

Where apple trees were thoroughly sprayed with one or more applications of lead arsenate after July 1, the amount of lead residue usually exceeded the present tolerance, 0.018.

When lead arsenate was used as late as the middle of June and some substitute insecticide was used for later applications, the lead residue was near the present tolerance.

When the use of lead arsenate was confined to the petal-fall spray, followed by one cover spray the first week of June, the lead residue was well within the tolerance.

The lead residue increased in proportion to the number of cover sprays containing lead arsenate applied after July 1.

When oil was used as a supplement to lead arsenate in the first or first and second cover sprays, no appreciable increase in lead residue at harvest time resulted.

The substitution of calcium arsenate for lead arsenate in the late summer sprays always resulted in diminishing the amount of lead, but this was not accompanied by a significant reduction in arsenic residue as compared with plots where lead arsenate was used throughout the season.

On plots sprayed with lead arsenate throughout the season there were generally a little more than twice as many grains of lead as of arsenic residue at harvest time.

Heavy rainfall during the late summer and early fall of 1935 may have aided in reducing the total load of residue but not sufficiently to make any practical difference in meeting the Federal tolerances.

Washing the apples once in the under brush flood type washer using either 1 or 1½ per cent acid solution almost invariably reduced the lead residue well within the present Federal tolerances even from plots which had received seven cover sprays.

Heating the washing solution increased its efficiency.

The addition of a wetting agent to cold acid solution had no appreciable effect on its efficiency but it did increase the efficiency of the heated solution.

The flotation washer was satisfactory for removing residue in nearly all cases but was considerably less efficient than the under brush flood type.

Russetting of the skin of Jonathan apples resulted in a heavier deposit of residue and also made removal more difficult.

The mechanical brush did not prove satisfactory for removing spray residue.

Sodium silicate used in connection with the regular lead arsenate midsummer spray resulted in serious injury to the foliage of Baldwin trees. Sodium silicate applied a week before harvest reduced the residue but not enough to avoid the need for washing apples which had received a late July application of lead arsenate.

Tandem washing is not required for the removal of residue under Ohio conditions.

Washing did not injuriously affect the keeping quality of the fruit.

The cost of washing, not including labor, was about 3 cents per bushel.

#### LITERATURE CITED

1. Association of Official Agricultural Chemists. 1930. Official and Tentative Methods of Analysis. Compiled by the Committee on Editing Methods of Analysis, Washington, D. C.
2. Burkholder, C. L. and O. W. Ford. 1935. Notes on 1934 apple washing which are of special interest to Indiana growers. *Hoosier Horticulture* 17: 83-89.
3. Diehl, H. C., D. F. Fisher, Henry Hartman, J. R. Magness, and R. H. Robinson. 1929. Removal of spray residue from northwest apples and pears in the Pacific Northwest. *U. S. D. A. Cir.* 59.
4. Ellenwood, C. W. 1936. Spray residue removal. *Ohio Agr. Exp. Sta. Spec. Cir.* 48.
5. Frear, Donald E. H. and D. E. Haley. 1934. A simplified method for the rapid determination of lead residues on apples. *Pa. Agr. Exp. Sta. Tech. Bull.* 304.
6. ——— and W. S. Hodgkiss. 1936. Accuracy of the determination of lead and arsenic on apples. *Jour. Agr. Res.* 52: 639-644.
7. ——— and H. N. Worthley. 1935. Study of the removal of spray residues from apples. *Jour. Agr. Res.* 51: 61-74.
8. ——— and ———. 1935. Removal of spray residues from apples. *Pa. Agr. Exp. Sta. Bull.* 318.
9. Groves, Kermit, R. E. Marshall, F. L. Overley, and J. L. St. John. 1936. The removal of fluorine spray residue from apples sprayed with natural cryolite. *Wash. Agr. Exp. Sta. Bull.* 329.
10. Haller, M. H., Edwin Smith, and A. L. Ryall. 1935. Spray residue removal from apples and other fruits. *U. S. D. A. Farmers' Bull.* 1752.
11. Hough, W. S., R. H. Hart, W. B. Ellett, J. F. Eheart, and A. B. Groves. 1931. Removal of spray residue from apples. *Va. Agr. Exp. Sta. Bull.* 278.
12. ———. 1936. Spray residues and their removal from apples. *Va. Agr. Exp. Sta. Bull.* 302.



13. Marshall, Roy E., F. L. Overley, and Kermit Groves. 1936. The relation of washing treatments to subsequent losses of moisture from apples. Wash. Agr. Exp. Sta. Bull. 330.
14. Porter, Stanley. 1936. How Lawrence County apple growers are handling the apple spray residue situation. Ohio State Hort. Soc. An. Rept., pp. 21-29.
15. Robinson, R. H. and M. B. Hatch. 1933. The removal of lead and arsenic spray residues from apples and pears. Oregon Agr. Exp. Sta. Bull. 317.
16. Streeter, L. R., P. J. Chapman, S. W. Harman, and G. W. Pearce. 1932. Spray and other deposits on fruit. N. Y. Agr. Exp. Sta. Bull. 611.
17. Wichmann, H. J., C. W. Murray, M. Harris, R. A. Clifford, J. H. Loughrey, and F. A. Vorhes Jr. 1934. Methods of determining lead in foods. Jour. Off. Agr. Chemists 17: 108-135.